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Multiple climate cooling prior to Sturtian glaciations: Evidence from chemical index of alteration of sediments in South China

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Investigation of climatic conditions prior to the Sturtian glaciations is critical to understanding the trigger mechanism for the series of Neoproterozoic global glaciations. In this study, we report high-resolution chemical index of alteration (CIA) records in the sediments of South China prior to the Sturtian glaciation (820~720 Ma). Our results showed there occurred multiple climate cooling before the Sturtian glaciations in South China: (1) a series of episodic and possibly global climate cooling periods from ca. 750 Ma to 725 Ma, which also caused some diachronous regional glaciations; (2) a permanent climate cooling period between ca. 800 Ma and 770 Ma, probably contemporaneous to the global "Bitter Springs stage" $\delta^{13}C$ negative excursion; (3) a climate cooling period between ca. 815 Ma and 810 Ma. The three stages of climate cooling are also supported by their correspondence to previously reported extremely low $\delta^{18}O$ records of igneous/metamorphic minerals from South China. These climate cooling periods also coincide with the magmatism and rifting events in South China. We argue that tectonic movements were the primary control on the climate cooling before the Neoproterozoic global glaciations.

Two globally extensive glaciations occurred during the Neoproterozoic era, with the Sturtian followed by the Marinoan, and 726 Ma is considered as the maximum constraints of the initiation of the Sturtian glaciation[1]. Various mechanisms have been proposed for the trigger of the Neoproterozoic global glaciations, mostly based on mathematical simulations[2–4]. These models, however, have yet to be verified by field evidence. In practical terms, systematic and high-resolution records of climate changes before the Sturtian glaciations remain largely unexplored.

It was suggested that multiple glaciations could have occurred prior to the Sturtian glaciations. Some diamictites prior to the Sturtian glaciations in Africa and Northwest China have been considered synchronous and indicative of a "Kaigas glaciation" roughly between 755 Ma and 735 Ma[5–8], but the chronological studies showed that these diamictites may be of different ages[1]. Extremely low $\delta^{18}O$ values (−14‰~−8‰) were documented in various minerals (e.g. garnet, zircon, and magnetite) from igneous/metamorphic rocks in South China at ca. 812 Ma, 780 Ma and 750 Ma, supporting continental glaciations at these ages during which glacial melt water participated in the mineral formations[9–11].

The major-element geochemistry and mineralogy of siliciclastic sediments are strongly affected by chemistry weathering, which leaches and subsequently depletes the soluble elements Ca, Na, and K relative to refractory element Al, and forms smectite and Al-bearing clay minerals in the residual materials[12–14]. Therefore, the chemical index of alteration (CIA) values of sediments could record the intensity of chemical weathering and associated climate conditions[12,14]. Generally, low CIA values indicate nearly absence of chemical alteration, pointing to a cold-arid climatic condition. Sparse low CIA values from the "pre-Sturtian" sediments in South China were reported, suggesting some short periods of climate cooling[15–18]. However, in the absence of reliable and high-resolution stratigraphic correlations, these diamictites, oxygen isotope and CIA records are hardly assembled, let alone the corresponding climate changes and their magnitudes.

We report a continuous and high-resolution chemostratigraphic record of the "pre-Sturtian" strata in South China focusing on the CIA profile, which provides a reliable proxy for the intensity of chemical weathering and associated climate conditions during the sedimentation events. The results show a complete profile of climatic variations during the "pre-Sturtian" era in South China, and put constraints on the trigger mechanism of Neoproterozoic glaciations in a global scale.

Results

Geological setting. Chang'an and Nantuo diamictite successions in South China are two well-developed Neoproterozoic glacial sequences. The Chang'an glaciation is constrained between ca. 725 Ma[19] and ca. 667 Ma[20], and the termination of Nantuo glaciation is constrained at ca. 635 Ma[21]. The chronological constraints indicate that these two glacial sequences are correlated to the Sturtian and Marinoan glaciations, respectively[22]. The interglacial Fulu and Datangpo Formation are sandwiched between these two glacial sequences.

The "pre-Sturtian" Xiajiang Group is part of the continuously deposited formations in Nanhua Rift basin, eastern Guizhou Province. Xiajiang Group was deposited between ca. 820 Ma and ca. 725 Ma[19,23,24] and is in conformable contact with the overlying Chang'an Formation. It is composed of Jialu, Wuye, Fanzhao, Qingshuijiang, Pinglve, and Longli Formations.

The Lijiapo section is located in Congjiang, southeastern Guizhou Province (Fig. 1), where is in the northwest of the center of Nanhua rift basin[25]. In this area, Xiajiang Group was deposited in slope to outer-shelf facies, and Chang'an, Fulu, and Nantuo Formation were deposited in inner-shelf to littoral facies[25,26]. The strata from Jialu to Nantuo formations consist of siliciclastic rocks, which are mainly composed of protolith clay minerals and quartz, with a few sericites and chlorites due to recrystallization. The stratigraphic column and lithological characteristics of each Formation are shown in Figure 2, in which the Datangpo Formation is too thin to be shown.

Availability of CIA for the climatic changes. The CIA values show significant stratigraphic variations from Jialu Formation to Nantuo Formation (Fig. 2, Supplementary Table S1), notably multiple negative excursions (NE1~NE8). These negative excursions would be like to suggest multiple climate cooling. However, the CIA values may be also affected by properties of parent rocks, sorting during transportation, and sediment conditions, etc[27]. Only for a sedimentary basin that develops under the similar sediment routing systems and source rocks, the variation of CIA values of sedimentary clastic rocks can be used to probe the variation of paleoclimate.

To avoid the CIA alteration by sorting process during transportation and deposition, only fine-grained samples were chosen for paleoclimate discussion, while coarse sandstones in Fulu Formation are excluded (Fig. 2). Furthermore, Zr/Sc–Th/Sc plots suggest that the samples were derived from discrete igneous sources, and the overall low Zr/Sc ratios (<25) indicate that sediment recycling did not significantly influence the chemical composition of the samples[28–30] (Supplementary Fig. S1 and Table S2). Therefore, samples from our study are considered as the products of a first-order cycle from erosion to deposition without polycyclic reworking.

From Chang'an to Nantuo Formation, the study area shows inner-shelf to littoral deposition facies. This sequence was considered as the first sedimentary overlay of Nanhua rift basin, and the sedimentation was in a relatively peaceful mode[25,26]. The A-CN-K ternary diagrams also show that the provenance of Chang'an, Fulu and Nantuo Formation are uniformly close to granodiorite (Fig. 3). Under alike sedimentary environment and sharing similar materials provenances from Chang'an to Nantuo Formations, the two negative excursions NE8 and NE7 are therefore highly consistent with the prediction by the CIA principle as these two formations were corresponding to cold-arid Marinoan and Sturtian glaciations.

It should be noted that CIA negative excursions (NE1~NE6) in Xiajiang Group show similar or even lower CIA values in comparison to glacial NE8 and NE7 (Fig. 2). These lower CIA do not imply more intense cold-arid climatic conditions in pre-glaciation period,

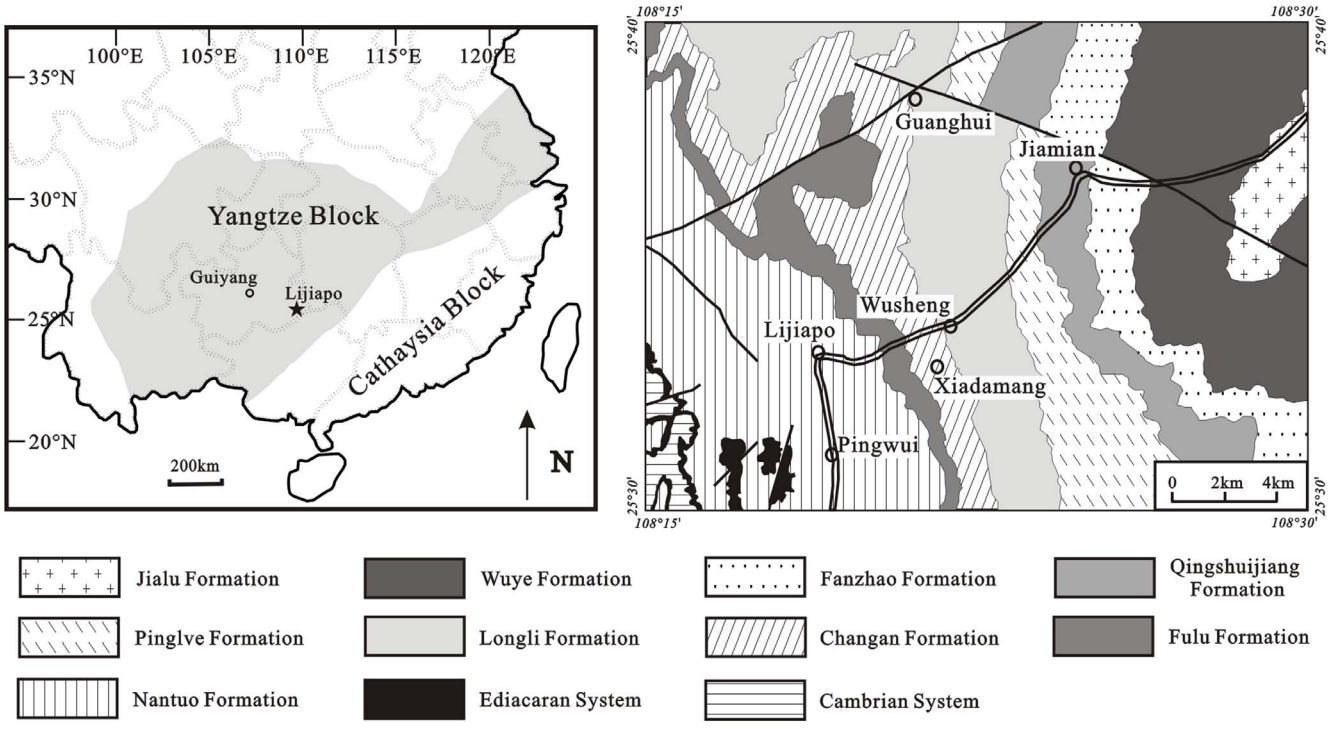

Figure 1 | Study region in the Yangtze Block of South China and geological map of Lijiapo section in eastern Guizhou Province. Modified from ref. 25.

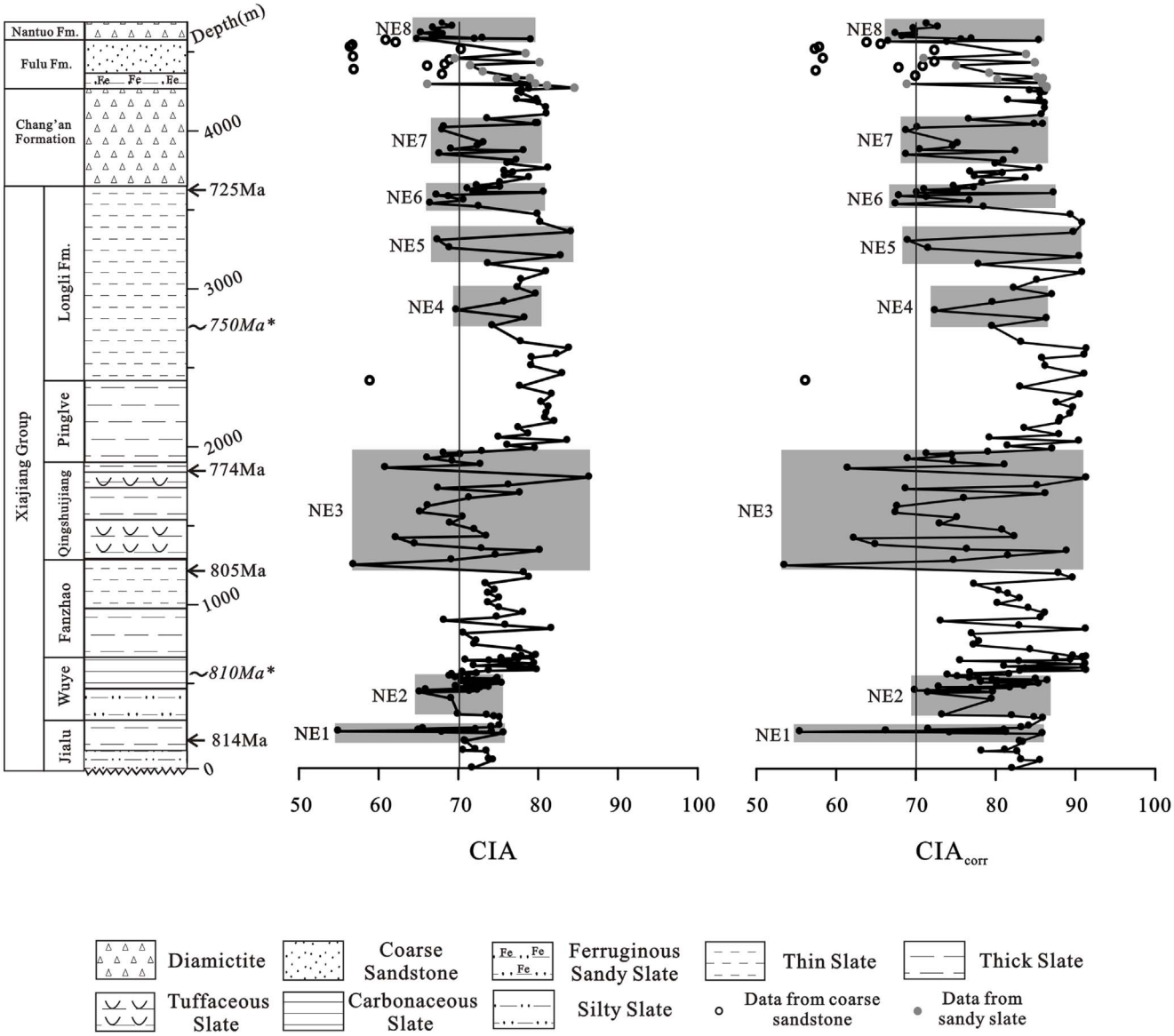

Figure 2 | Stratigraphic column and chemical index of alteration (CIA) variations from Jialu to Nantuo Formation in Lijiapo section. The normal chronology data is the published data from ref. 24, in which the chronology data are from the same Lijiapo sections. The italic chronology data with label "*" are estimated based on the strata thickness and sedimentation rate. CIA_{corr} indicates corrected CIA values for K-metasomatism; the CIA results from coarse sandstones are excluded during the discussions.

but rather represent different sediment conditions and source rocks. Xiajiang Group here deposited in slope to outer-shelf deposition facies, and is considered to occur as the rapid filling mode during the development of Nanhua rift basin[25,26]. The A-CN-K ternary diagrams show that the provenance of Xiajiang Group are uniformly close to tonalite rather than granodiorite (Fig. 3).

Obviously, the CIA of the pre-glacial sediments cannot be compared with that of glacial sediments in a quantitative way. However, as we discussed above, the sediment conditions and source rocks of pre-glacial Xiajiang Group did not change much, and the sediments of Xiajiang Group are uniform and fine-grained, indicating the similar sorting effect. Under the same background, consequently, stratigraphic CIA variations within Xiajiang Group could represent the paleoclimate changes. In other words, the negative excursions of CIA in Xiajiang Group would least imply relatively climate cooling during "pre-Sturtian" period.

Low CIA and climate cooling during pre-glaciation period. From the middle of Longli Formation to the base of Chang'an Formation, the CIA values show three negative excursions (NE4, NE5, and NE6) (Fig. 2), supporting a series of alternately cooling and warming episodes. New chronological data from tuffaceous bed constrain the top of Qingshuijiang Formation at the age of ca. 774 Ma[24], and the NE4, NE5, and NE6 would be roughly constrained between 750 Ma and 725 Ma (Fig. 2). Feng et al.[16] and Wang et al.[18] reported low CIA (about 55~70) of Liantuo Formation (ca. 748 Ma at the lower part) in Hubei Province, also supporting climate cooling at ca. 750 Ma in South China.

Some glacial or marine-glacial records prior to the Sturtian glaciations were reported in Africa and Northwest of China, including the Kundelungu glaciation in Zambia roughly between 765 ± 5 Ma and 735 ± 5 Ma[7], the older glaciation of Port Nolloth Group in southwest Namibia between 752 ± 6 Ma and 741 ± 6 Ma[5,6], and the Beiyixi diamictites in northwest China between 740 ± 7 Ma and 725 ± 10 Ma[8]. The Beiyixi Formation sediments also show very low CIA values (about 51~65)[31]. These glaciations spanned a long time roughly from ca. 760 Ma to 725 Ma, and are hardly to be integrated as a unified "Kaigas glaciation". With the addition of current study,

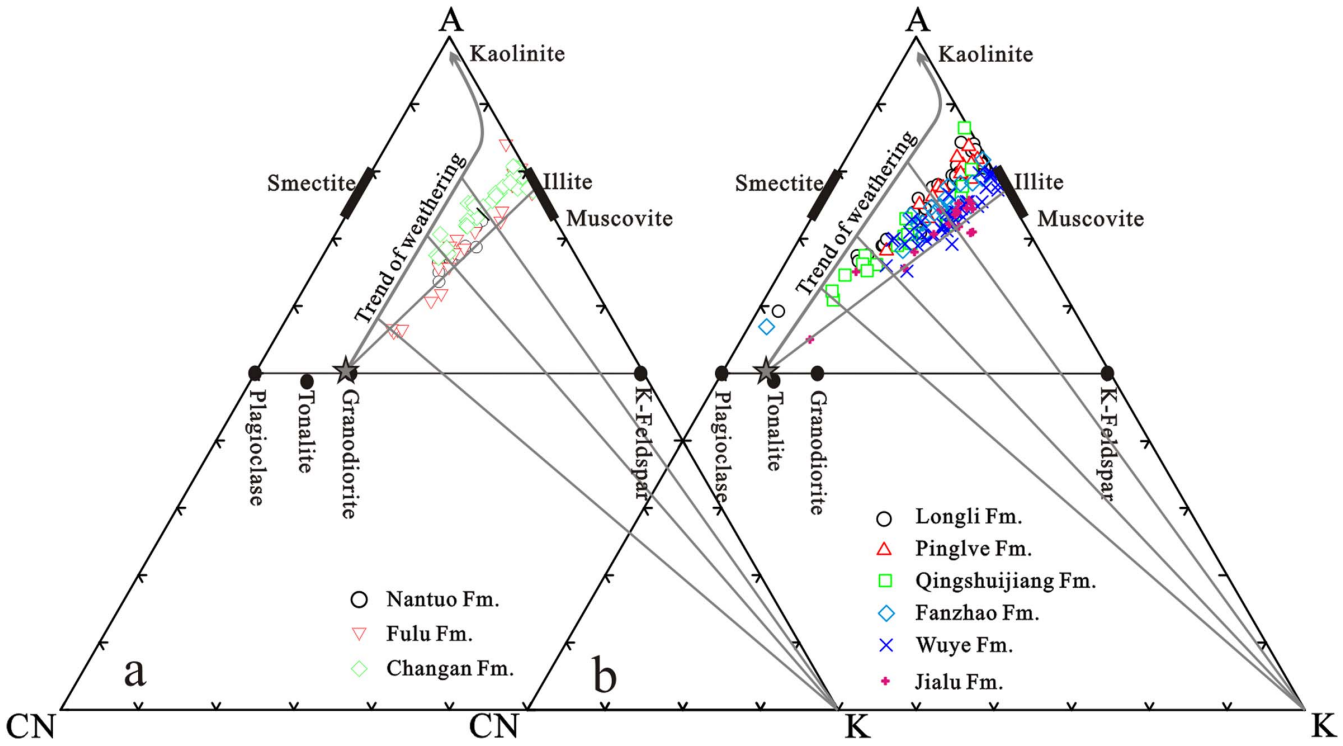

Figure 3 | A-CN-K (Al_2O_3-CaO* + Na_2O-K_2O) ternary diagrams of the samples from Lijiapo section.

we argue that multiple climate cooling episodes occurred globally between ca. 750 Ma and 725 Ma. Although the climate was not severe enough to yield synchronous glaciations globe wide, special conditions (e.g. the high altitude) could produce numerous regional glaciations within the 25 Myrs (ca. 750 to 725 Ma) time window.

The CIA decrease and keep in low values from the top of Fanzhao Formation to the base of Pinglve Formation in NE3 (Fig. 2). The top of Qingshuijiang Formation is constrained at the age of ca. 774 Ma, and the top of Fanzhao Formation is constrained at the age of ca. 805 Ma[24]. Thus, NE3 suggests a long climate cooling period between 800 Ma and 770 Ma. Feng et al.[15] also reported low CIA values (60~70) roughly between 758 ± 23 Ma and 809 ± 16 Ma from the Xieshuihe Formation in Hunan Province, South China[32]. These CIA records imply climate cooling between ca. 800 Ma and 770 Ma in South China.

A pronounced $\delta^{13}C$ negative excursion was reported from the "pre-Sturtian" Neoproterozoic strata in northeastern Svalbard, northwestern Canada, and Australia, which is called "Bitter Springs stage" with $\delta^{13}C$ values decreasing from >5‰ to about −4‰ roughly between 800 Ma and 780 Ma[33–35]. The large shifts in $\delta^{13}C$ of Neoproterozoic seawater might be associated with regional glaciation, but supporting evidence for this argument have not been found in any basin of this age[33]. The NE3 excursion in our study might provide such an evidence for the global climate cooling between 800 Ma and 770 Ma.

NE1 and NE2 show low CIA values in the upper part of Jialu Formation and the lower part of Wuye Formation respectively (Fig. 2). The middle of Jialu Formation is constrained at the age of 814 ± 6 Ma[24], and we argue that NE1 and NE2 indicate climate cooling between ca. 815 Ma and 810 Ma.

Chen et al.[9], Zheng et al.[11,36] and Tang et al.[10] reported extremely low $\delta^{18}O$ values (−14‰~−8‰) in various minerals (e.g. garnet, zircon, and magnetite) from the Neoproterozoic igneous/metamorphic rocks along the Dabie-Sulu orogenic belt in South China. SHRIMP U–Pb dating for zircons (or coexisting zircons) yields three groups of ages at ca. 812 Ma, 780 Ma and 750 Ma. These extremely low $\delta^{18}O$ values of igneous minerals were interpreted as crystallizing from negative $\delta^{18}O$ magmas due to melting of meteoric-hydrothermally altered negative $\delta^{18}O$ rocks, suggesting contemporaneous continental glaciations in South China[10,11]. However, there are not any synchronous glaciations records yet found in South China, and Bindeman[37] and Wang et al.[38] argued that glacial meltwater might not necessarily be required to explain the extremely low $\delta^{18}O$. In their model, mid-latitude meteoric precipitation (rain or snow) could be isotopically light enough to introduce the low silicate $\delta^{18}O$, but the meteoric precipitation with $\delta^{18}O$ low to −11‰ would still require mean annual temperature close to 0°C. Therefore, the extremely low $\delta^{18}O$ in igneous/metamorphic minerals reflect cold climate despite the involvement of glacier or meteoric waters. The CIA results in this study suggest three stages of climate cooling in South China roughly during 815~810 Ma, 800~770 Ma, and 750~725 Ma respectively, which are correlated with the ages of extremely low $\delta^{18}O$ values (812 Ma, 780 Ma and 750 Ma) very well. We suggest that the CIA results and extremely low negative $\delta^{18}O$ values together strongly support that multiple episodes of climate cooling between ca. 820 Ma to 725 Ma.

Discussion

Regional climate cooling would be controlled by the changes of latitude and altitude. The global paleogeographic reconstructions show that South China block was located in located in 40° N~60° N at ca. 825 Ma, 10° S~10° N at ca. 780 Ma, 20° N~40° N at ca. 750 Ma, 20° N~40° N at ca. 720 Ma[39,40], which do not show any correlation to the multiple climate cooling events. In addition, no evidence supports large-scale orogenic movement that would markedly change the altitude in South China during this period. Therefore, the climate cooling events may be caused by the reduction of greenhouse gases or block of solar radiation, which would be affected by the tectonic movements.

Li et al.[39] suggested that broad mantle upwellings (or superplumes) beneath the Rodinia supercontinents lead to widespread bimodal magmatism (including plume magmatism) and continental rifting between ca. 825 Ma and 740 Ma, resulting in the complete break-up of Rodinia supercontinents by 570 Ma. Evidence in South China

feature four major episodes of magmatism and rifting in the ca. 830–700 Ma interval: ca. 820 Ma, ca. 800 Ma, ca. 780 Ma, and ca. 750–720 Ma[39], which are close to or coincident with the multiple climate cooling events.

The tectonic movements of Rodinia supercontinents may have caused climate cooling through following major processes: (1) break-up of a supercontinent into several smaller plates would increase in the sources of moisture along continental borders, resulting in an increase of precipitation and runoff over the continental masses, which would enhance continental silicate weathering[2]; (2) magmatism (e.g. plume magmatism) would produce large basaltic provinces, resulting in an increase of the weather ability of the continental surface[41,42]; (3) increase in explosive volcanism would continuously inject sulfur aerosols into the stratosphere[43]. Processes (1) and (2) could lower atmospheric carbon dioxide concentration, and process (3) could disrupt Earth's radiative balance, all of which could cause climate cooling. Importantly, Donnadieu et al.[2] used a coupled climate–geochemical model to assess the effects of the paleogeographic and tectonic changes before the global glaciations, and the simulation results showed that the process (1) was most effective on climate cooling.

From 820 Ma to 725 Ma, rifting produced very limited new continental borders, so process (1) was restricted. Thus, episodes of magmatism and rifting would cause climate cooling by process (2) and (3). When the surface temperature was low enough, weathering of silicate rock would have largely slowed down, which might prevent further development of climate cooling[44]. Then the accumulation of CO_2 from volcanic outgassing for millions years would transform the climate condition from an 'icehouse' to a 'greenhouse'. This process could explain the cooling-warming cycles before 725 Ma. Li et al.[40] suggested that the onset of Rodinia breakup likely occurred at ca. 720 Ma, when South China started to break away. This process produced several smaller plates and abundant continental borders that significantly enhanced the CO2 consumption from the atmosphere. In this case, process (1) yielded the greatest effects on climate cooling, which might trigger the runaway albedo and lead to the initiation of global glaciations from ca. 720 Ma. Our hypothesis is subject to further testes by field observations and numerical models.

Methods

210 fresh sedimentary rock samples are collected continuously from the base of Jialu Formation to the lower part of Nantuo Formation at Lijiapo section. All the samples show good-gained except the coarse sandstone. Specifically, the size of most grains are less than 0.01 mm for other samples (including matrix of diamictite, sandy slate and slate). Some grains in sandy slate do not show very fine, but their size are also less than 0.05 mm.

All the fresh samples were trimmed to remove any weathered surfaces and then ground into powder (<200 mesh) using a tungsten carbide mill. After being roasted at 1000°C for an hour, samples powder was mixed with $Li_2B_4O_7$ in 1 : 5 weight ratio. The mixtures were then melted at 1100°C, and made for fusion glasses for analysis. Major elements were analyzed by an automatic X-ray fluorescence spectrometer (PW2404) using these fusion glasses in the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. Analytical precision for major element concentrations is generally better than 3%. The chemical index of alteration (CIA) is calculated as follows: CIA = molar $[(Al_2O_3)/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$, where the measured values are expressed as molar proportions, and CaO* represents the CaO in silicate minerals only[12]. CaO* can be corrected by the formula: CaO* = mol CaO − mol $CO_{2\ calcite}$ − mol $CO_{2\ dolomite} \times 1/2$ − mol $P_2O_{5\ apatite} \times 10/3$[12,45]. In our most samples, CaO was initially corrected for phosphate using available P_2O_5 data (CaO* = mol CaO−mol $P_2O_5 \times 10/3$) due to the low carbonate content (Supplementary Fig. S2). If the remaining number of moles is less than that of Na_2O, the CaO value was adopted as the CaO*. Otherwise, the CaO* was assumed to be equivalent to Na_2O[13].

Some of the analyzed rocks have undergone low-degree of metamorphism, which were considered that would not cause considerable changes of CIA values[12]. K-addition to aluminous product and K-substitution for Ca/Na in plagioclase during diagenesis would alter primary weathering trends of the sediments (Supplementary Fig. S3). All the samples are plotted in the A-CN-K ternary diagrams (Fig. 3). The provenance of samples of the Nantuo, Fulu and Chang'an Formation are close to granodiorite, whereas samples from underneath the Chang'an Formation are close to tonalite. The effects of K-metasomatism can be removed by extending a vector from the K_2O apex through each sample on the A-CN-K (Al_2O_3-CaO* + Na_2O-K_2O) diagrams[45,46]. Specifically, K_2O addition to each sample can be calculated according to: $K_2O_{corr} = [m \times A + m \times (C^* + N)]/(1 - m)$ (Equation 1)[46]. In this equation, m = K/(A + C* + N + K) for the parent sample (protolith), and A, (C* + N) and K are molar values of Al_2O_3, (CaO* + Na_2O) and K_2O, respectively. The "prealteration" K_2O value can be calculated by using Equation 1. Using K_2O_{corr}, the corrected CIA (CIA_{corr}) can be recalculated as follows: CIA_{corr} = molar $[(Al_2O_3)/(Al_2O_3 + CaO^* + Na_2O + K_2O_{corr})] \times 100$.

For a comparison, both CIA corrected values (CIA_{corr}) and uncorrected values are all illustrated in Figure 2 and Supplementary Table S1. Figure 2 show that K-metasomatism changed the primary CIA values, but the CIA_{corr} and CIA show similar stratigraphic variations, indicating the similar trends of climate changes.

~20 mg of sample powder was weighed and ashed at 450°C for 12 h. Then the ashed sample dissolution was carried out using a three acid (i.e., HNO_3, HF, and HCl) digestion. The solution were subsequently analyzed by a PerkinElmer DRCII ICP-MS at University of Science and Technology of China. Based on duplicate analysis, the analytical precision is better than 8% for all of the analyzed trace metals and rare earth elements.

The backscattered electron (BSE) microscopic photos were taken on a Tescan Mira 3 LMH FE-SEM at University of Science and Technology of China, with a beam current of 20 nA and an acceleration voltage of 15 kV. The map was obtained using a dwell time of 200 ms per pixel, a resolution of 1024 × 800 pixels for the map and the area per pixel is ~2.9 μm × 2.9 μm.

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Author contributions

J.H. and X.C. designed research; J.H., L.F., D.L. and Q.Z. performed research; J.H. and L.F. analyzed data; J.H., L.F., T.S. and X.C. wrote the paper.

Additional information

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